DIVISION S-6—SOIL & WATER MANAGEMENT & CONSERVATION

GLEAMS, Opus, PRZM2β, and PRZM3 Simulations Compared with Measured Atrazine Runoff

Qingli Ma, James E. Hook,* R. Don Wauchope, Clyde C. Dowler, A. W. Johnson, Jessica G. Davis, Gary J. Gascho, Clint C. Truman, Harold R. Sumner, and Lawrence D. Chandler

ABSTRACT

High-intensity storms that occur shortly after chemical application have the greatest potential to cause chemical runoff. We examined how effectively current chemical transport models GLEAMS, Opus, PRZM2β, and PRZM3 could predict water runoff and runoff losses of atrazine [6-chloro-*N*-ethyl-*N*′-(1-methylethyl)-1,3,5-triazine-2,4-diamine] under such conditions, as compared with observations from a controlled field runoff experiment. The experiment was conducted for 2 yr using simulated rainfall on two 14.6- by 42.7-m plots within a corn (*Zea mays* L.) field on Tifton loamy sand (fine-loamy, kaolinitic, thermic Plinthic Kandiudults) under conventional tillage practices. For each plot-year, atrazine was applied as surface spray immediately after planting and followed by a 50-mm, 2-h simulated rainfall 24 h later. A similar preapplication rainfall and four subsequent rainfalls during the growing season were also applied. Observed water runoff averaged 20% of the applied rainfall. Less runoff occurred from freshly tilled soil or under full canopy cover; more runoff occurred when nearly bare soil had crusted. Observed total seasonal atrazine runoff averaged 2.7% of that applied, with the first posttreatment event runoff averaging 89% of the total. GLEAMS, Opus, PRZM2β and PRZM3 adequately predicted water runoff amounts, with normalized root mean square errors of 29, 29, 31, and 31%, respectively. GLEAMS and PRZM3 predicted atrazine concentrations in runoff within a factor of two of observed concentrations. PRZM2β overpredicted atrazine concentrations. Opus adequately predicted atrazine concentrations in runoff when it was run with an equilibrium adsorption submodel, but significantly underestimated atrazine concentrations when it was run with a kinetic sorption submodel.

Pesticide runoff from agricultural fields is greatest when heavy rainfall occurs shortly after soil surface pesticide applications (Wauchope, 1978; Leonard, 1990; Squillace and Thurman, 1992). Although this kind of scenario is infrequently observed on any given site, storms that cause significant amounts of surface runoff are common in the southeast Coastal Plains and southern Piedmont. Given the extensive area that is treated with pesticides in this region, particularly during the months of March, April, and May, it is likely that a storm of sufficient magnitude to cause surface water runoff will occur on some fields that have recently been treated with pesticides.

Field studies of pesticide runoff typically depend on the occurrence of natural rainfall because simulated rainfall cannot be generated at hectare and larger scales. Micro-scale plots (microplots), typically 5 to 50 m^2, are commonly used with rainfall simulators. While valuable in specific pesticide transport studies, microplots are thought to overestimate pesticide runoff as compared with typical field studies. This is more likely due to the severe conditions often used in microplots (Wauchope et al., 1995; Wauchope and Burgoa, 1995). Moreover, microplots cannot adequately represent typical agricultural management practices and the major characteristics of a typical field. In the early 1990s, Coody et al. (1990, 1994) developed a rainfall simulator for use on intermediate-scale plots, typically 500 m^2, sometimes referred to as “mesoplots.” This equipment made it feasible for worst-case pesticide runoff studies at near field scale.

Perhaps the most useful role of mesoplot studies is to test chemical transport models for a variety of scenarios. Simulation models are efficient analytical tools to evaluate the effects of various agricultural management practices on surface and ground water quality. They are especially valuable for predicting system behavior under a wide range of conditions that may be economically or technically impossible to investigate by experiment. Two models, GLEAMS and PRZM, have been applied extensively for pesticide leaching predictions (Carsel et al., 1985, 1986; Leonard et al., 1987; Sauer et al., 1990; Willian et al., 1999; Zacharias and Heatwole, 1994; Malone et al., 1999); however, they have not been adequately evaluated for severe or “worst-case” scenarios. Applications of Opus are rather recent, with a focus on water and chemical leaching (Smith, 1995). Our objective was to evaluate the performance of GLEAMS (ver-

Q.L. Ma, USDA-ARS, U.S. Salinity Lab, Soil Physics and Pesticide Research Unit, 450 West Big Springs Rd., Riverside, CA 92507; J.E. Hook and G.J. Gascho, Dep. of Crop and Soil Sciences, Univ. of Georgia, P.O. Box 748, Tifton, GA 31793-0748; R.D. Wauchope, A.W. Johnson, and C.C. Dowler, USDA-ARS Nematodes, Weeds, and Crops Research Unit, H.R. Sumner, USDA-ARS Insect Biology and Pest Management Research Unit; C.C. Truman, USDA-ARS Southeast Watershed Research Unit, P.O. Box 748, Tifton, GA 31793-0748; J.G. Davis, Dep. of Soil and Crop Sciences, Colorado State Univ., Fort Collins, CO 80524; L.D. Chandler, USDA-ARS National Grain Insect Research Lab., Brookings, SD 57006-9803. Research supported by USDA-CSREES-NRI. Received 21 June 1999. *Corresponding author (jimhook@tifton.cpes.peachnet.edu).

Published in Soil Sci. Soc. Am. J. 64:2070–2079 (2000).

Abbreviations: GLEAMS, Groundwater Loading Effects of Agricultural Management Systems; Opus, An Integrated Simulation Model for Transport of Non-Point Source Pollutants at the Field Scale; PRZM, Pesticide Root Zone Model. PRZM2β and PRZM3 are β-test version 2 and version 3 of PRZM, respectively.

Table 1. Means ($n = 24$) of measured soil and soil hydraulic properties of the major diagnostic horizons of Tifton loamy sand at the Abraham Baldwin Agricultural College research farm.

Depth	Sand	Silt	Clay	OC†	θ_{sat}†	θ_{33}†	θ_{1500}†	ρ†	K_s^a†	K_s^g†
m	%				$m^3\ m^{-3}$			$Mg\ m^{-3}$	$cm\ h^{-1}$	
0.00 to 0.29	84.6	9.3	6.1	0.79	0.381	0.141	0.047	1.64	18.7	12.1
0.29 to 0.62	63.4	11.4	25.2	0.34	0.362	0.215	0.149	1.69	8.75	4.54
0.62 to 0.92	62.9	11.0	26.1	0.24	0.373	0.257	0.162	1.66	12.7	3.52
0.92 to 1.11	62.3	10.6	27.1	0.12	0.366	0.259	0.177	1.68	6.02	3.35
1.11 to 1.43	60.4	11.8	27.8	0.02	0.362	0.281	0.187	1.69	1.71	0.49
1.43 to 1.60	48.3	15.8	35.9	0.01	0.377	0.291	0.224	1.65	2.01	0.19

† Organic carbon; θ_{sat}, θ_{33} and θ_{1500} are volumetric soil water content at 0-, 33- and 1500-kPa suctions, respectively; ρ is soil bulk density; and K_s^a and K_s^g are the arithmetic and geometric means of saturated hydraulic conductivity, respectively.

sion 2.10), Opus (version 1.9), PRZM2β, and PRZM3 models for predicting atrazine runoff under severe rainfall conditions. Predictions of surface water runoff by GLEAMS, Opus, and PRZM2 were reported earlier (Ma et al., 1998). They were included here to compare with those predicted by PRZM2β and PRZM3. We included surface water runoff also because atrazine runoff is closely related to water runoff.

MODEL DESCRIPTION

Detailed descriptions of GLEAMS, Opus, PRZM2β, and PRZM3 models have been presented elsewhere (Carsel et al., 1998; Leonard et al., 1987; Smith, 1992). Briefly, GLEAMS estimates surface water runoff on the basis of the Soil Conservation Services (SCS) curve number method driven by daily rainfall, with modifications that relate the curve number to daily soil water content in the root zone (Williams and Nicks, 1982). The PRZM2β and PRZM3 models also use curve number method, but relate the curve number to soil moisture limits in the surface zone (top 0.3 m) (Haith, 1979). The soil moisture limits are calculated from soil water content in the surface zone and are simplified to match the three antecedent soil moisture conditions based on 5-d antecedent rainfall by SCS (USDA-SCS, 1972). In these associations, a 1-cm difference in soil water storage is assumed among the three soil moisture limits. In Opus, the user can select an infiltration-based runoff model which requires detailed breakpoint rainfall input, or a modification of the SCS curve number method as that used in GLEAMS (Williams and Nicks, 1982; Williams et al., 1984). We used the daily hydrology option.

GLEAMS, PRZM2β, and PRZM3 use a "tipping bucket" approach for calculation of water flow downward in the soil profile, which is based on soil layer field capacity (33 kPa suction), wilting point (1500 kPa suction), and saturation point. Opus simulates water retention and hydraulic characteristics using a modification of the Brooks-Corey functions (Brooks and Corey, 1964; Smith, 1992).

All four models assume first-order decay for pesticide dissipation. GLEAMS and PRZM2β ignore the effects of temperature and soil water content on pesticide decay. PRZM3 uses a Q_{10} parameter, which is the increase of degradation rate with 10°C increase in temperature, to describe temperature-dependent degradation. Also, both PRZM2β and PRZM3 can simulate pesticide biodegradation using a model developed by Soulas (1982). However, there is not much evidence that this biodegradation model has been frequently used because of the extensive data requirements. Opus uses the pesticide degradation model developed by Walker (1974) to describe temperature- and moisture-dependent degradation. Opus also accounts for the effect of microbial activity on pesticide decay by assuming that the decay rate below the microbial-active zone (about 0.2 m) is a user-defined fraction of the surface soil decay rate.

All models assume that pesticide adsorption follows a linear, instantaneous equilibrium adsorption isotherm described by:

$$C_s = K_d C_l \qquad [1]$$

where C_l (mg L^{-1}) and C_s (mg kg^{-1}) are pesticide concentrations in solution and on adsorbed phase, respectively. K_d (L kg^{-1}) is the pesticide equilibrium adsorption coefficient, which is chemical- and site-dependent. K_d is often related to K_{oc} (L kg^{-1}), the normalized equilibrium adsorption constant on soil organic C content, which is primarily chemical-dependent (Chiou et al., 1979).

Opus has an option to describe pesticide sorption by a kinetic sorption submodel, which assumes that pesticide concentrations in the adsorbed phase change with time in proportion to the extent of the non-equilibrium. This process is described by:

$$\frac{dC_s}{dt} = \nu(C_l K_d - C_s) \qquad [2]$$

where t (h) is time, and ν (h^{-1}) is a kinetic sorption

Table 2. Actual rainfall amounts for simulated rainfall events measured using catch-up cups and rain gauges.

Plots	1	2	3	4	5	6
	Measured rainfall amount† (mm) — Simulated rainfall events					
			1992			
A	49.95 ± 0.55 (40–59)	52.81 ± 0.64 (43–61)	51.72 ± 0.73 (41–67)	52.27 ± 0.60 (43–61)	50.0	50.0
B	53.48 ± 0.71 (44–64)	51.65 ± 0.48 (46–59)	50.32 ± 0.55 (37–60)	51.63 ± 0.61 (42–63)	50.0	50.0
			1993			
A	50.74 ± 0.68 (39–61)	52.50 ± 0.54 (46–61)	51.20 ± 0.57 (43–59)	52.27 ± 0.60 (43–61)	50.0	50.0
B	49.37 ± 0.61 (40–58)	50.43 ± 0.69 (41–61)	52.91 ± 0.59 (42–61)	48.51 ± 1.72 (40–69)	50.0	50.0

† Mean plus standard error. Values in parentheses are range of measured rainfall amount (mm).

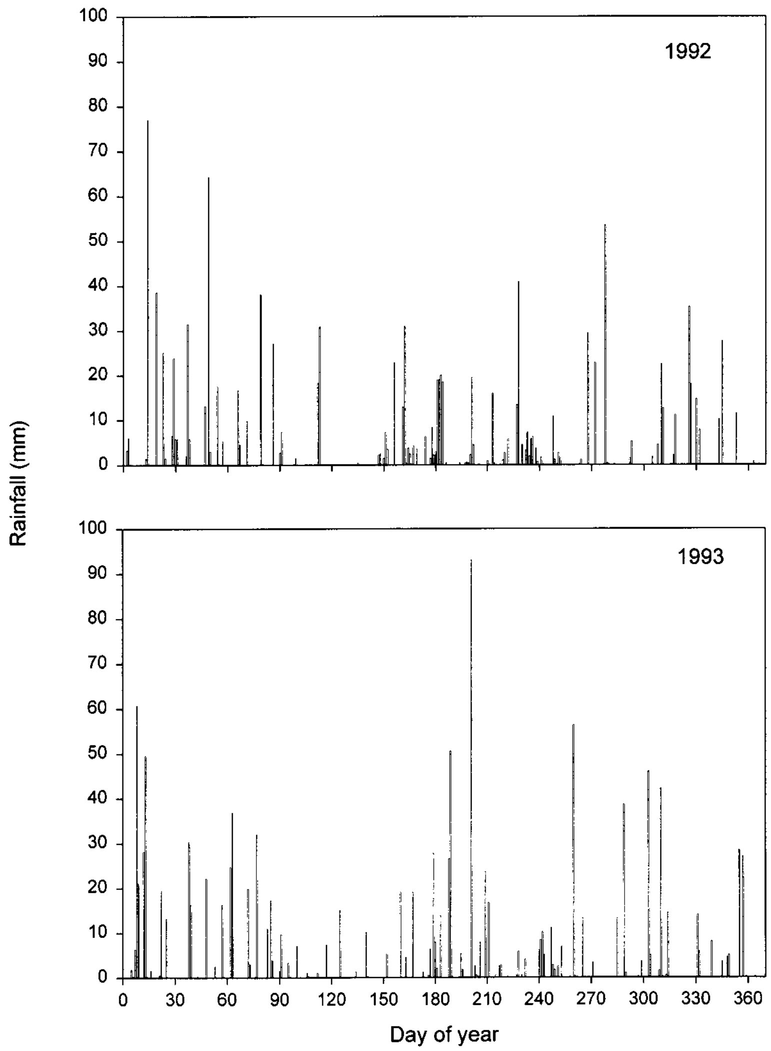

Fig. 1. Daily natural rainfalls for the experimental site for 1992 and 1993.

rate coefficient. Note that this kinetic sorption model is different from a two-site or bi-continuum sorption model in which a fraction of the sorption sites is in instantaneous equilibrium while the rest of the sites are in kinetics (Rao et al., 1979; Brusseau and Rao, 1991; Ma et al., 1995; Ahuja et al., 1996).

In GLEAMS, PRZM2β, and PRZM3, the amount of pesticide runoff is calculated from water runoff volumes, empirical extraction coefficients, and pesticide concentrations within the surface layer of the soil, assuming a fixed mixing depth at the soil surface. For GLEAMS, the mixing depth is 10 mm. For PRZM2β, it is the topmost, user-defined soil layer, usually 10 mm or less. For PRZM3, a nonuniform mixing submodel (Ahuja, 1986) is used in which the mixing depth is 20 mm and the extent of mixing decreases exponentially with depth. Opus uses an effective mixing depth which is a user-defined fraction of the top 10-mm soil layer.

The crop growth models employed by GLEAMS, Opus, PRZM2β, and PRZM3 are empirical in nature. Processes such as major management practices and tillage operations are explicitly defined in GLEAMS and Opus. While in PRZM2β and PRZM3, optional "special actions" allow for users to assign new values to some time-dependent variables for a specified period of time. These variables include runoff curve number, soil bulk density, and pesticide adsorption coefficient. This feature of PRZM2β and PRZM3 can be used to calibrate the effects of management practices and soil surface cover on model variables.

MATERIALS AND METHODS

Field Experiment and Runoff Collection

Detailed description of the field experimental design has been reported elsewhere (Sumner et al., 1996; Ma et al., 1998; Wauchope et al., 1999). Briefly, two 14.6- by 42.7-m plots (A and B) were defined within a field in 1992. Tillage and corn management followed normal practices for the region. The field was disked twice to a 15-cm depth in January; deep-turned to 30 cm with a moldboard plow, and the beds shaped with a light harrow in April; see Wauchope et al. (1999) for further details. Each plot had eight 1.8-m wide beds divided by wheel tracks. Each bed had two rows of corn 0.9 m apart. Plots were separated from each other and from the outside

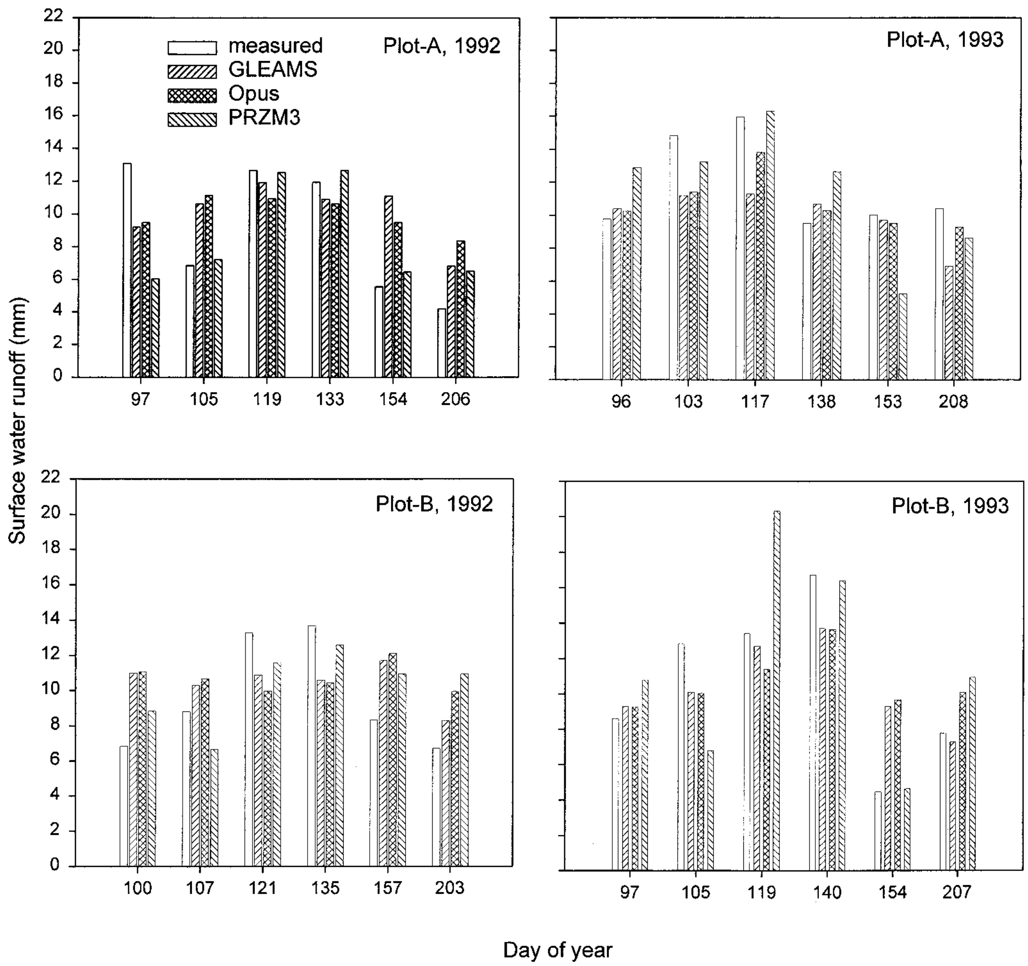

Fig. 2. Measured and predicted surface water runoff by GLEAMS, Opus, and PRZM3 models during 2 yr of corn growing seasons from two mesoplots on the Tifton loamy sand from 1992 to 1993.

areas by 18 m with soil preparation and corn management as within the plots. The soil was Tifton loamy sand with 3% of slope parallel to the rows.

Soil properties were obtained from 24 pedon samples taken along four down-slope transects of the plots. Saturated hydraulic conductivity was measured with undisturbed cores (60-mm i.d., 89-mm height) by the constant head method of Klute and Dirksen (1986), with the modifications suggested by Hill and King (1982). These cores were then used for measuring soil bulk density and water retention characteristics. Soil water content at 33 and 1500 kPa suctions were measured in pressure chambers from loose soil. Particle size distribution and organic carbon content were determined by the methods of Day (1965) and Walkley-Black (Nelson and Sommers, 1982), respectively. These values are summarized in Table 1.

Six simulated rainfalls (25 mm h^{-1} for 2 h each) were applied to each plot at times ranging from preplanting to full canopy cover, using a mesoplot rainfall simulator (Sumner et al., 1996) in each of 2 yr 1992 and 1993. A rainfall amount and intensity of this magnitude occurs with a return frequency of approximately once per year in the southeastern USA, based on our analysis of 15-min rainfall records from 1985 to 1994 (data not shown). Each plot was irrigated separately as an independent unit. Seventy-two catch-up cups (90-mm i.d., 140-mm height) and two standard rain gauges were used to measure actual rainfall intensity and amount (Table 2) for all but the last two simulated rainfall events for which the fully developed canopy interfaced with the measurements. Event 1 occurred 1 d after moldboard plowing and shaping soil beds 7 d before planting each year. Event 2 occurred 1 d after rototilling, planting, and atrazine application (downdraft spray broadcast onto the surface applying 1.87 kg atrazine ha^{-1} in 370 L water ha^{-1}). This occurred on Day 105 and 107 in 1992 and on Days 103 and 105 in 1993 for the first and second replicates, respectively. Event 2 is effectively a worse-case or severe scenario for atrazine runoff. Events 3 and 4 occurred with sparsely covered canopy and crusted soil surface 14 d and 28 d after planting, respectively. Events 5 and 6 occurred with full corn canopy 50 and 100 d after planting, respectively.

Surface runoff was measured with a flume and bubble pressure recording depth meter (Wauchope et al., 1999). Only runoff from simulated rainfall events was measured during the entire period of study. Runoff samples were analyzed for atrazine using high performance liquid chromatography or gas chromatography. Daily climatic data including natural rainfall (Fig. 1), temperature, radiation, wind speed, relative humidity, and pan evaporation were measured near the site. Simulated rainfall was combined with measured natural rainfall on that day as the daily total in model predictions. Crop-related model inputs including dates of emergence, maturity and harvest and plant height at maturity (2.2 m) were measured on the site. Plant uptake of atrazine was ignored for all models because corn was still very small when atrazine concentration in runoff solution went below the analytical detection limit of 1.0 μg

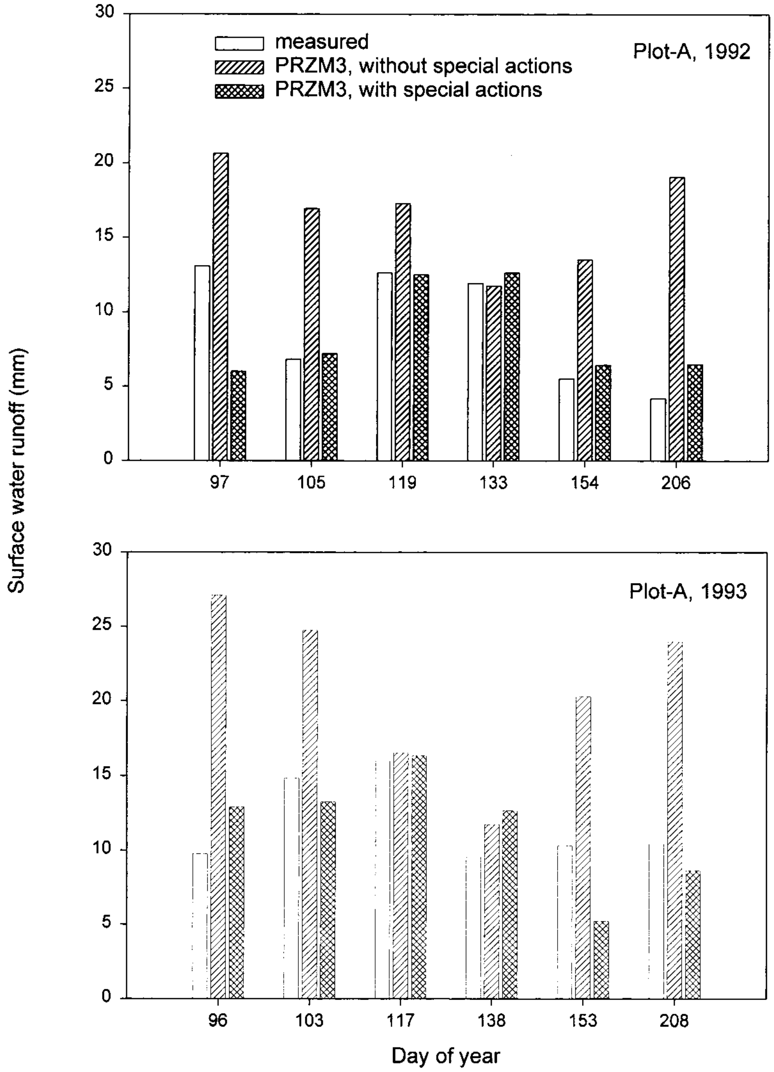

Fig. 3. Effects of the 'special actions' options on surface water runoff predictions by PRZM3.

L^{-1}. The erosion simulations were also ignored. This would not cause noticeable influence on atrazine runoff predictions since 99% of atrazine runoff occurred in solution (Kenimer et al., 1987; Pantone et al., 1992; Basta et al., 1997).

Parameterization of GLEAMS, Opus, PRZM2β, and PRZM3

Soil water retention data were fitted by the modified Brooks and Corey functions (Brooks and Corey, 1964; Smith, 1992) to obtain the Brooks and Corey parameters and soil water contents at saturation (0 kPa), at field capacity (33 kPa), and at wilting point (1500 kPa). A curve number of 85 was reported for a nearby site on a similar soil (Knisel et al., 1991), and through sensitivity analysis on the same hydrology data as used in the current study, this value was found to give acceptable runoff predictions (Ma et al., 1998). This value for Tifton loamy sand on the experimental site is complicated by surface crusting and sealing and transient perched water conditions at subsurface horizons. The "special actions" feature of PRZM2β and PRZM3 were used to modify the soil surface conditions caused by canopy development. The modified parameter was curve number which had a new value of 69 starting on 1 June of each year when full corn canopy (1.2-m tall corn) was developed. This value was obtained by minimizing the differences between measured and predicted water runoff using data collected from plot-A in 1992. Therefore, this modification is a calibration process. An effective rooting depth of 1.1 m for corn was chosen due to a flow-restricting layer starting at this depth (Table 1). The modified Penman-Monteith combination equations (Jensen et al., 1990) in GLEAMS and the Penman equation in Opus were used for estimating potential evapotranspiration. For PRZM2β and PRZM3, measured pan evaporation was used.

Values for soil organic carbon sorption constant for atrazine (100 L kg^{-1}), and atrazine dissipation half-life in the field soil (60 d) were obtained from a previous study on the site (Ma et al., 1996). The activation energy (34.6 kJ mol^{-1}) required by Opus was obtained from Rocha and Walker (1995).

Sensitivity Analysis

Sensitivity analysis in the current study is focused on the effective mixing depth for chemical transfer to surface runoff and the kinetic sorption rate coefficient. These parameters are difficult to measure but may be important for accurate

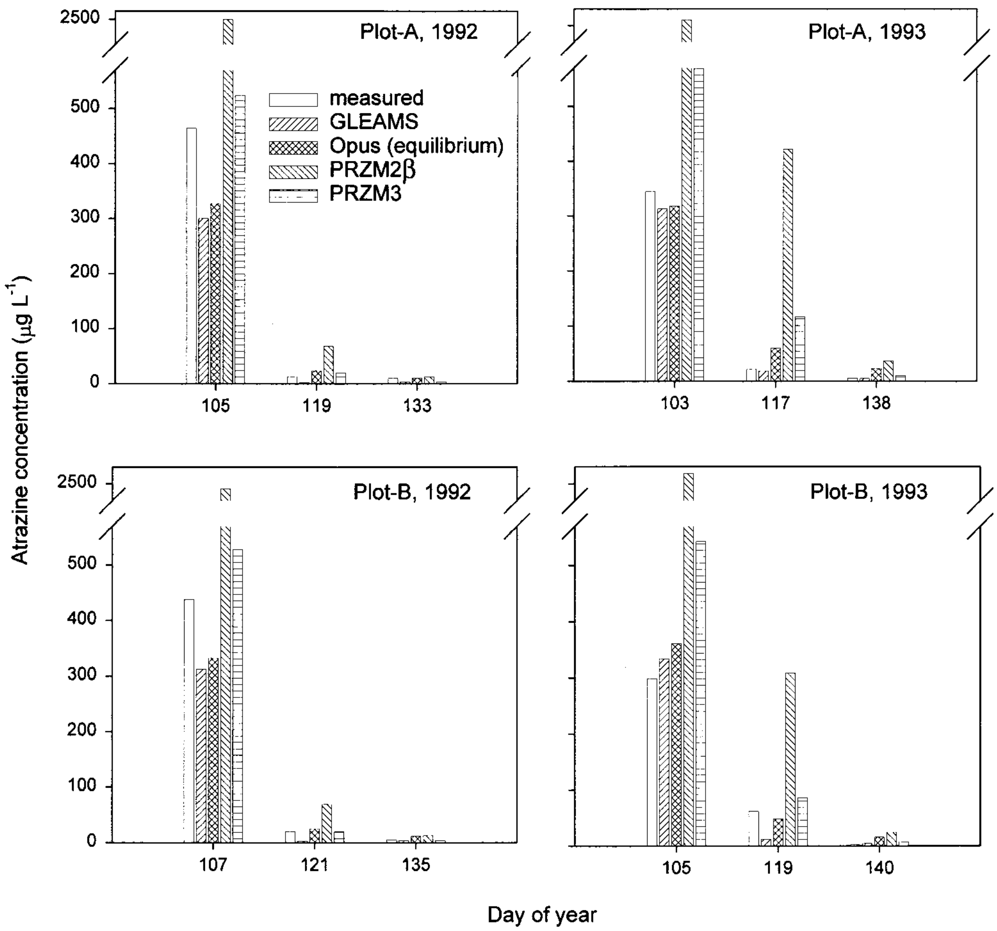

Fig. 4. Measured and predicted atrazine concentrations in runoff solution by GLEAMS, Opus, PRZM2β and PRZM3 during 2 yr of corn growing seasons from two mesoplots on the Tifton loamy sand from 1992 to 1993.

runoff predictions. Sensitivity of the model predictions to soil hydraulic parameters was presented by Smith (1993) for Opus for a set of assumed scenarios and by Ma et al. (1998) for GLEAMS, Opus and PRZM2 using the same hydrology data as used in this study. Therefore, they are not repeated here. Briefly, runoff predictions by all models were very sensitive to curve number. In addition, runoff predictions by GLEAMS and PRZM were also sensitive to soil water contents at field capacity and wilting point. The geometric mean and arithmetic mean of the measured K_s were compared using the Opus model to examine their influences on runoff predictions, as both means were reported in the literature.

Criteria for Goodness of Fit

The normalized root mean square error (Loague and Green, 1991), which counts errors of both overpredictions and underpredictions, was used for evaluations of surface water runoff. A paired *t*-test was also used where applicable since this test does not require an equal variance assumption. We used the commonly accepted criterion proposed by Parrish and Smith (1990), that acceptable model predictions should be within a factor of two of the measurements, for atrazine runoff evaluations. This criterion was originally proposed for evaluating model predictions for chemical concentration profiles in soils, but it is equally applicable for comparing pesticide concentrations in runoff. We accepted a 0.05 level of significance unless otherwise specified.

RESULTS AND DISCUSSION

Measured and Predicted Surface Water Runoff

Measured surface water runoff from all 24 runoff events for the four plot-years, reported previously by Ma et al. (1998), was compared (Fig. 2). The runoff observed at different times over the seasons reflects the effects of tillage operations, surface crusts and seals, corn canopy, and rainfall and runoff history on runoff generation. Measured water runoff averaged 20% of the applied rainfall overall. Events 1 and 2 generated less runoff because these events occurred on freshly tilled soil with a high infiltration rate. Events 3 and 4 had high runoff because the soil was crusted, greatly reducing infiltration rate. Runoff decreased for Events 5 and 6 because the growing corn canopy increasingly intercepted rainfall and caused "stem flow."

Runoff predicted by GLEAMS, Opus (Ma et al., 1998), PRZM2β[1], and PRZM3 generally followed the seasonal pattern of the observations (Fig. 2). Since PRZM2β predicted the same surface water runoff as

[1]Simulations were also run for a previous version of PRZM, PRZM2 (Mullins et al., 1993). PRZM2 predicted different water runoff than did PRZM2β (Ma et al., 1998), which essentially predicted the same runoff as PRZM3.

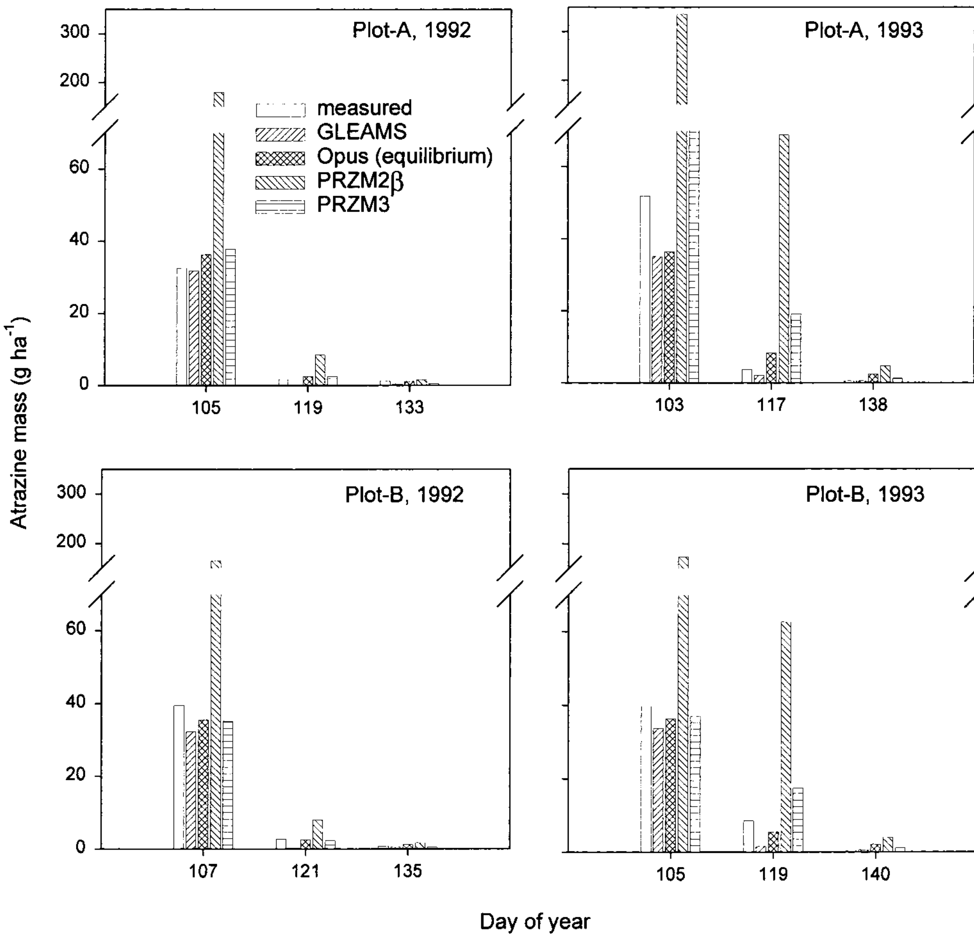

Fig. 5. Measured and predicted atrazine mass losses in runoff solution by GLEAMS, Opus, PRZM2β and PRZM3 during 2 yr of corn growing seasons from two mesoplots on the Tifton loamy sand from 1992 to 1993.

PRZM3, it was eliminated from Fig. 2. The normalized root mean square error (NRMSE) for the 24 events was 29% for GLEAMS, 29% for Opus, and 31% for PRZM2β and PRZM3 (with the "special actions" feature implemented, see below). Thus, all four models reasonably simulated water runoff.

When individual event predictions are compared with observations, GLEAMS and Opus generally overpredicted runoff when measured runoff was low and underpredicted runoff when it was high. This is primarily a result of limitations imposed by the curve number method which lumps the most important factors controlling runoff, namely seasonal changes in canopy development and soil conditions. PRZM2β and PRZM3 better predicted high and low runoff, when the 'special actions' feature of the models was used to correct for the effect of canopy cover on runoff predictions. Without this correction, both PRZM2β and PRZM3 predicted a very different runoff pattern over the season, as is shown in Fig. 3 for Plot A in 1992 and 1993. Similar results were obtained for other plot-years (not shown).

Since the arithmetic mean K_s (K_s^a) was significantly greater ($P = 0.02$) than the geometric mean K_s (K_s^g) for all soil horizons (Table 1), Opus predicted more runoff when K_s^g was used than when K_s^a was used. However, the differences in runoff predictions were not statistically significant ($P = 0.63$), and the calculated NRMSEs were 29% using either K_s^a or K_s^g. Thus Opus was not sensitive to K_s when the daily hydrology option was used. These results are consistent with those of a previous study (Ma et al., 1998). Therefore, K_s^g is used in the remaining Opus simulations.

Measured and Predicted Atrazine Concentrations and Loads in Runoff

Since all four models gave reasonable simulations of water runoff, we proceeded with comparison of atrazine runoff (Fig. 4). Measured atrazine concentrations in runoff were above the analytical detection limit of 1.0 μg L^{-1} for the first three runoff events after atrazine application, and only these events are used for atrazine comparisons. For runoff events which occurred 1 d after atrazine application (first post-treatment events), the average of the ratios of GLEAMS-predicted to measured atrazine concentrations in runoff was 0.85, indicating that GLEAMS reasonably predicted atrazine concentrations for these runoff events on the basis of the Parrish and Smith's "within 2×" criterion. For runoff events occurring later in the season, the ratio of GLEAMS-predicted to the measured atrazine concentrations in runoff varied between 0.15 and 1.73. Larger

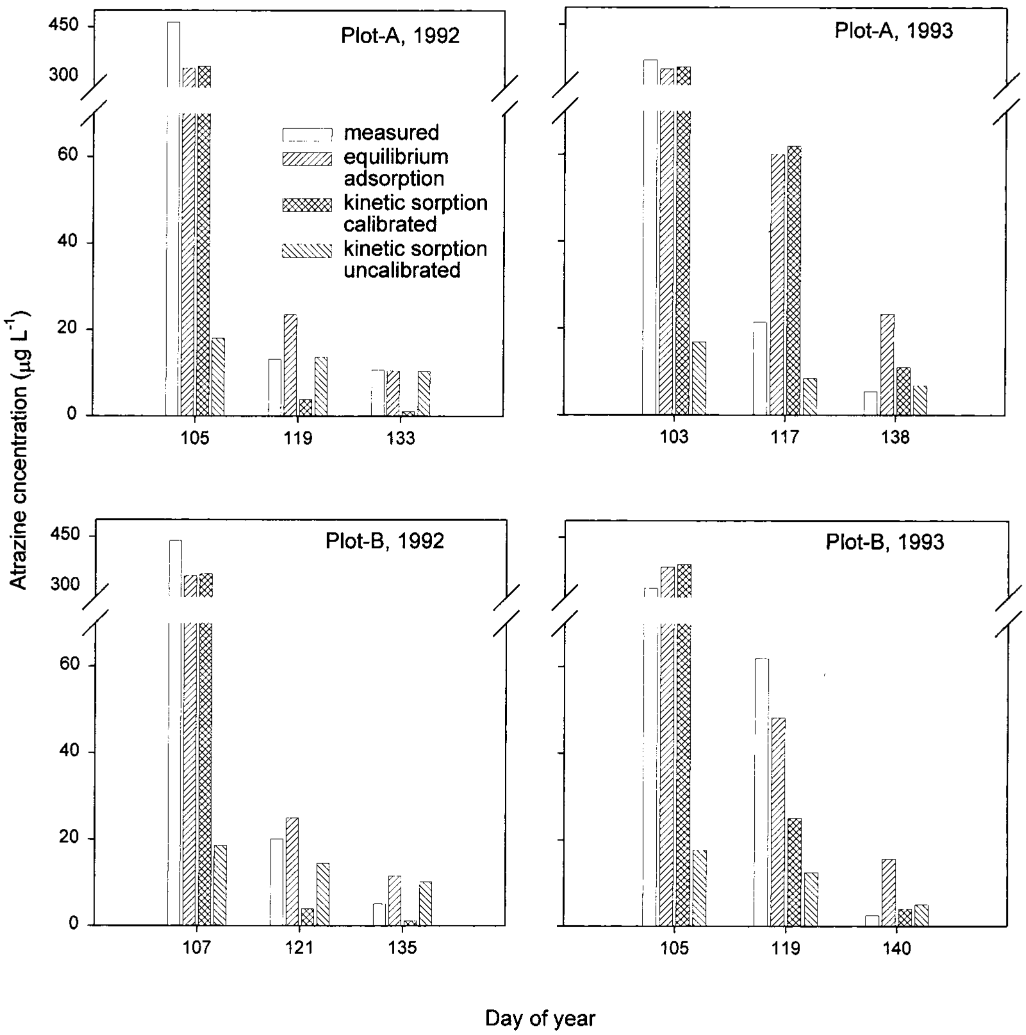

Fig. 6. Measured and Opus-predicted atrazine concentrations in runoff solution with equilibrium adsorption submodel as compared with uncalibrated and calibrated kinetic sorption submodel.

deviations occurred mostly during the second runoff event after atrazine application. The average ratio over all postapplication events was 0.72.

With the linear equilibrium adsorption submodel (Eq. [1]), Opus reasonably simulated atrazine concentrations in runoff (Fig. 4), especially for the first posttreatment events: the ratios of the predicted to the measured concentrations averaged 0.9. The ratio varied between 0.76 and 6.26 over all runoff events with an average of 2.0.

PRZM2β and PRZM3 use very different methods for calculating chemical transfer to runoff and predicted different chemical concentrations in runoff. For PRZM2β, the average of the ratios of predicted to the measured atrazine concentrations in runoff was 5.84 for first posttreatment events and the average was 6.72 over all runoff events. Thus, PRZM2β generally overpredicted atrazine concentrations. Since the mixing depth for atrazine transfer to runoff was the same for GLEAMS and PRZM2β and since both models adequately predicted surface water runoff, the overpredictions by PRZM2β suggest that the extraction coefficient for the chemical transfer to runoff, a value that is fixed specifically for a group of chemicals in the model, is too large. A sensitivity analysis for PRZM2β for the mixing depth demonstrated that the model would still significantly overpredict atrazine runoff when the mixing depth was reduced by 2-fold to 5.0 mm (not shown). This supports the conclusion that the model's default extraction coefficients were too large.

For PRZM3, the average of the ratios of predicted to the measured atrazine concentrations in runoff was 1.46 for the first posttreatment events and varied between 0.35 and 5.48 over all runoff events with an average of 1.73. Therefore, PRZM3 adequately predicted atrazine concentrations and the nonuniform mixing submodel employed in PRZM3 appears to have considerably improved predictions as compared with the uniform mixing submodel in PRZM2β.

Measured seasonal atrazine runoff load averaged over the four plot-years was 2.7% of the amount applied. The maximum in any plot-year was 3.3%. These values are consistent with field-scale studies (Wauchope, 1978; Basta et al., 1997). Predicted seasonal loads were 2.1% by GLEAMS, 2.5% by Opus (with equilibrium adsorption), 15.0% by PRZM2β, and 3.4% by PRZM3. When compared for individual runoff events between observations and model predictions, the errors in atrazine mass loss predictions are similar in trend to those in concentrations (Fig. 5). Except for PRZM2β, these are excellent results. Measured atrazine runoff from the first posttreatment events averaged 89% of the seasonal total. It is clear that agricultural management practices desired for controlling pesticide runoff losses should focus on these early runoff events. GLEAMS, Opus (with equilibrium adsorption), PRZM2β, and PRZM3 predicted that 96, 85, 84, and 83% of the total atrazine runoff were in the first post-application events, respectively.

Opus' runoff predictions, using both calibrated and uncalibrated kinetic sorption submodel, are compared with observations and predictions using the equilibrium adsorption submodel (Fig. 6). The kinetic sorption rate used ($\nu = 0.011$ h^{-1}) was obtained independently by fitting atrazine breakthrough curves from packed soil from the site (Ma et al., 1996). With the uncalibrated kinetic sorption submodel, Opus does not adequately simulate atrazine concentrations in runoff (Fig. 6). Atrazine load in runoff was predicted as 0.3% of that applied, significantly less than that measured (2.7%). Opus also predicted that 46% of the total atrazine runoff occurred in the first posttreatment runoff events, instead of 89% as measured. We conducted an extensive sensitivity analysis for ν in relation to atrazine runoff predictions (not shown). With ν values ranging from 0.002 h^{-1} for slow pore water velocity to 0.03 h^{-1} for fast pore water velocity (Gaber et al., 1995), we could not achieve reasonable predictions. The ν value (0.011 h^{-1}) that we obtained by curve-fitting procedure was the same as that obtained by Gaber et al. (1995) at medium pore water velocity (0.01 h^{-1}). Only with an unreasonably small ν value (1×10^{-7} h^{-1}) obtained by model calibration using measured atrazine runoff concentrations from Plot A in 1992, could atrazine runoff for the first post-treatment events be reasonably simulated with the kinetic sorption submodel (Fig. 6). Furthermore, even with such a small ν value, atrazine runoff for the second post-treatment events was poorly simulated. Therefore, we think that the kinetic sorption submodel is not applicable for the conditions studied.

SUMMARY AND CONCLUSIONS

Observed surface water runoff followed a trapezoidal pattern across the entire corn-growing season, whereas concentrations of atrazine in surface runoff decreased rapidly. The first posttreatment runoff events always carried the highest amount of atrazine, averaging 89% of the total atrazine runoff. Seasonal runoff of atrazine averaged 2.7% of that applied. This percentage is consistent with typical field studies on atrazine runoff, indicating that pesticide runoff data collected from mesoplot studies are realistic and could be used for management and decision-making. The GLEAMS, Opus, PRZM2β and PRZM3 models reasonably predicted surface water runoff. Under the same hydrologic conditions and applying the "within 2×" criterion for adequate predictive performance, atrazine concentrations and loads in the first post-treatment events were adequately predicted by GLEAMS, Opus (with equilibrium adsorption) and PRZM3, but greatly overpredicted by PRZM2β. Poor predictions by PRZM2β are presumably due to an unrealistic mixing model, which has been substantially corrected in PRZM3 by use of the nonuniform mixing model of Ahuja (1986).

REFERENCES

Ahuja, L.R. 1986. Characterization and modeling of chemical transfer to runoff. Adv. Soil Sci. 4:149–188.

Ahuja, L.R., Q.L. Ma, K.W. Rojas, J. Boesten, and H.J. Farahani. 1996. A field test of the Root Zone Water quality model—pesticide and bromide behavior. Pestic. Sci. 48:101–108.

Basta, N.T., R.L. Huhnke, and J.H. Stiegler. 1997. Atrazine runoff from conservation tillage systems: A simulated rainfall study. J. Soil Water Conserv. 52:44–48.

Brooks, R.H., and A.T. Corey. 1964. Hydraulic properties of porous media. Hydrology paper 3, Colorado State University, Fort Collins, CO.

Brusseau, M.L., and P.S.C. Rao. 1991. Sorption kinetic of organic chemicals: Methods, models, and mechanisms. *In* Rates of soil chemical processes. SSSA Spec. Publ. 27. SSSA, Madison, WI.

Carsel, R.F., J.C. Imhoff, P.R. Hummel, J.M. Cheplick, and A.S. Donigian, Jr. 1998. PRZM-3, Model for predicting pesticide and nitrogen fate in the crop root and unsaturated soil zones: Users manual for release 3.0. USEPA, Athens, GA.

Carsel, R.F., L.A. Mulkey, M.N. Lorber, and L.B. Baskin. 1985. The pesticide root zone model (PRZM): A procedure for evaluating pesticide leaching threats to ground water. Ecol. Model. 30:49–69.

Carsel, R.F., W.B. Nixon, and L.G. Ballantine. 1986. Comparison of pesticide root zone model predictions with observed concentrations for the tobacco pesticide matalaxyl in unsaturated zone soils. Environ. Toxicol. Chem. 5:345–353.

Chiou, C.T., L.J. Peters, and V.H. Freed. 1979. A physical concept of soil-water equilibria for nonionic organic compounds. Science 206:831–832.

Coody, P.N., and L.J. Lawrence. 1994. Method and system for collecting meso-scale rainfall simulations and collecting runoff. U.S. Patent No. 5279151. Date issued 18 Jan. 1994.

Coody, P.N., J.W. White, and R.L. Graney. 1990. A small plot approach to predicting pesticide runoff and aquatic exposure. Proc. Soc. Environ. Contam. Toxicol. 11th Annu. Mtg., Washington, DC. 11–15 November 1990.

Day, P.R. 1965. Particle fractionation and particle-size analysis. p. 545–565. *In* C.A. Black et al. (ed.) Methods of soil analysis. Part 1. 1st ed. Agron. Monogr. 9. ASA, Madison, WI.

Gaber, H.M., W.P. Inskeep, S.D. Comfort, and J.M. Wraith. 1995. Nonequilibrium transport of atrazine via large intact soil cores. J. Environ. Qual. 59:60–67.

Haith, D.A. 1979. Effect of soil and water conservation practices on edge-of-field nutrient losses. *In* D.A. Haith and R.C. Loehr (ed.) Effectiveness of soil and water conservation practices for pollution control. Section 6. USEPA Rep. 600/3-79-106. U.S. Gov. Print. Office, Washington, DC.

Hill, R.L., and L.D. King. 1982. A permeameter which eliminates boundary flow errors in saturated hydraulic conductivity measurements. Soil Sci. Soc. Am. J. 46:877–880.

Jensen, M.E., R.D. Burman, and R.G. Allen (ed.) 1990. Evapotranspiration and irrigation requirements. Manuals and reports on engineering practice. No. 70. Am. Soc. Civil Eng., New York.

Kenimer, A.L., S. Mostaghimi, R.W. Young, T.A. Dillaha, and V.O. Shanhiltz. 1987. Effects of residue cover on pesticide losses from conventional and no-tilliage systems. Trans. ASAE 30:953–959.

Klute, A., and C. Dirksen. 1986. Hydraulic conductivity and diffusivity: Laboratory methods. p. 678–734. *In* A. Klute (ed.) Methods of soil analysis. Part 1. 2nd ed. Agron. Monogr. 9. ASA, Madison, WI.

Knisel, W.G., R.A. Leonard, F.M. Davis, and J.M. Sheridan. 1991. Water balance components in the Georgia Coastal Plain: A GLEAMS model validation and simulation. J. Soil Water Conserv. 46:450–456.

Leonard, R.A. 1990. Movement of pesticides into surface waters. p.

303–349. *In* H.H. Cheng (ed.) Pesticides in the soil environment: Processes, impacts and modeling. SSSA Book Ser. No. 2. SSSA, Madison, WI.

Leonard, R.A., W.G. Knisel, and D.A. Still. 1987. GLEAMS: Groundwater loading effects of agricultural management systems. Trans. ASAE 30:1403–1418.

Loague, K.M., and R.E. Green. 1991. Statistical and graphical methods for evaluating solute transport models: Overview and applications. J. Contam. Hydrol. 7:51–73.

Ma, Q.L., L.R. Ahuja, K.W. Rojas, V.A. Ferreira, and D.G. DeCoursey. 1995. Measured and RZWQM predicted atrazine dissipation and movement in a field soil. Trans. ASAE 38:471–479.

Ma, Q.L., L.R. Ahuja, R.D. Wauchope, J.G. Benjamin, and B. Burgoa. 1996. Comparisons of equilibrium and equilibrium-kinetic sorption models for simulating simultaneous leaching and runoff of pesticides. Soil Sci. 161:646–655.

Ma, Q.L., R.D. Wauchope, J.E. Hook, A.W. Johnson, C.C. Truman, C.C. Dowler, G.J. Gascho, J.G. Davis, H.R. Sumner, and L.C. Chandler. 1998. GLEAMS, Opus and PRZM2 model-predicted versus measured water runoff from a coastal plain loamy sand. Trans. ASAE 41:77–88.

Malone, R.M., R.C. Warner, S.R. Workman, and M.E. Byers. 1999. Modeling surface and subsurface pesticide transport under three field conditions using PRZM-3 and GLEAMS. Trans. ASAE 42:1275–1287.

Mullins, J.A., R.F. Carsel, J.E. Scarbrough, and A.M. Ivery. 1993. PRZM2: A model for predicting pesticide fate in the crop root and unsaturated soil zones: Users manual for release 2.0. USEPA Rep. 600/R-93/046. Athens, GA.

Nelson, D.W., and L.E. Sommers. 1982. Total carbon, organic carbon, and organic matter. p. 539–579. *In* A.L. Page et al. (ed.) Methods of soil analysis. Part 2. 2nd ed. Agron. Monogr. 9. ASA, Madison, WI.

Parrish, R.S., and C.N. Smith. 1990. A method for testing whether model predictions fall within a prescribed factor of true values, with an application to pesticide leaching. Ecol. Model. 51:59–72.

Pantone, D.J., R.A. Young, D.D. Buhler, C.V. Eberlein, W.C. Koskinen, and F. Forcella. 1992. Water quality impacts associated with pre- and post-emergence applications of atrazine in maize. J. Environ. Qual. 21:567–573.

Rao, P.S.C., J.M. Davidson, R.E. Jessup, and H.M. Selim. 1979. Evaluation of conceptual models for describing non-equilibrium adsorption-desorption of pesticides during steady-flow in soil. Soil Sci. Soc. Am. J. 43:22–28.

Rocha, F., and A. Walker. 1995. Simulation of the persistence of atrazine in soil at different sites in Portugal. Weed Res. 35:179–186.

Sauer, T.J., K.J. Fermanich, and T.C. Daniel. 1990. Comparison of the pesticide root zone model simulated and measured pesticide mobility under two tillage systems. J. Environ. Qual. 19:727–734.

Smith, R.E. 1992. Opus: An integrated simulation model for transport of nonpoint-source pollutants at the field scale. ARS-98. Vol. 1. Documentation. USDA-ARS, Fort Collins, CO.

Smith, R.E. 1993. Simulated experiments on the role of soil hydraulic characteristics in agro-ecosystems. Model. Geo-Biosphere Processes 2:1–14.

Smith, R.E. 1995. Opus simulation of a wheat/sugarbeet plot near Neuenkirchen, Germany. Ecol. Model. 81:121–132.

Soulas, G. 1982. Mathematical model for microbial degradation of pesticides in the soil. Soil Bio. Biochem. 14:107–115.

Squillace, P.G., and E.M. Thurman. 1992. Herbicides transport in rivers—Importance of hydrology and geochemistry in nonpoint-source contamination. Environ. Sci. Technol. 26:538–545.

Sumner, H.R., R.D. Wauchope, C.C. Truman, C.C. Dowler, and J.E. Hook. 1996. Rainfall simulator and plot design for mesoplot runoff studies. Trans. ASAE 39:125–130.

USDA-SCS. 1972. Estimation of direct runoff from storm rainfall. p. 1–24. *In* U.S. Department of Agriculture, Soil Conservation Service, National Engineering Handbook: Hydrology. U.S. Gov. Print. Office, Washington, DC.

Walker, A. 1974. A simulation model for prediction of herbicide persistence. J. Environ. Qual. 3:396–401.

Wauchope, R.D. 1978. The pesticide content of surface water draining from agricultural fields—A review. J. Environ. Qual. 7:459–474.

Wauchope, R.D., and B. Burgoa. 1995. Pesticide runoff studies: toward a new protocol. p. 273–285. *In* M.L. Leng et al. (ed.) Agrochemical environmental fate studies: State of the art. CRC Press, Inc. Boca Raton, FL.

Wauchope, R.D., R.L. Graney, S. Cryer, C. Eadsforth, A.W. Klein, and K.D. Racke. 1995. Pesticide runoff: Methods and interpretation of field studies. Pure Appl. Chem. 67:2089–2108.

Wauchope, R.D., H.R. Sumner, C.C. Truman, A.W. Johnson, C.C. Dowler, J.E. Hook, G.J. Gascho, J.G. Davis, and L.D. Chandler. 1999. Runoff from a corn field as affected by tillage and corn canopy: A large scale simulated-rainfall hydrologic data set for model testing. Water Resour. Res. 35:2881–2885.

Williams, J.R., and A.D. Nicks. 1982. CREAMS hydrology model—Option 1. p. 69–86. *In* V.P. Singh (ed.) Applied modeling in catchment hydrology. Proc. of the Int. Symp. on Rainfall-Runoff Modeling. Water Resource Publications, Littleton, CO.

Williams, J.R., C.A. Jones, and P.T. Dyke. 1984. A modeling approach to determining the relationship between erosion and soil productivity. Trans. ASAE 27:129–144.

Willian, W.T., T.C. Mueller, R.M. Hayes, D.C. Bridges, and C.E. Snipes. 1999. Comparison of PRZM and GLEAMS computer model predictions with field data of fluometuron and norfluarozon behavior in soil. Weed Technol. 13:561–570.

Zacharias, S., and C.D. Heatwole. 1994. Evaluation of GLEAMS and PRZM for predicting pesticide leaching under field conditions. Trans. ASAE 37:439–451.